

# Crystal field in rare earth aluminates

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## Abstract

A method to calculate the crystal field parameters *ab initio* is proposed and applied to trivalent rare earth impurities in yttrium aluminate and to  $\text{Tb}^{3+}$  ion in  $\text{TbAlO}_3$ . To determine crystal field parameters local Hamiltonian expressed in basis of Wannier functions is expanded in a series of spherical tensor operators. Wannier functions are obtained by transforming the Bloch functions calculated using the density functional theory based program. The results show that the crystal field is continuously decreasing as the number of  $4f$  electrons increases and that the hybridization of  $4f$  states with the states of oxygen ligands is important. Theory is confronted with experiment for  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  ions in  $\text{YAlO}_3$  and for  $\text{Tb}^{3+}$  ion in  $\text{TbAlO}_3$  and a fair agreement is found.

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## I. INTRODUCTION

*Ab initio* calculations of the properties of molecules and solids became a common tool of solid states physics and quantum chemistry. Nevertheless there remain problems which are still not satisfactorily treated by the *ab initio* methods, one of these problems being description of the  $4f$  states of rare earth (R) atoms and ions. Providing that  $4f$  electrons are localized, the effective Hamiltonian method can be applied when analyzing the experimental results. Effective Hamiltonian depends on parameters, values of which must be fixed, however. To this end either the fit to experimental results may be used or the parameters must be estimated using semiempirical or *ab initio* methods.

Original motivation of this work was to explain the physics of magnetic rare earth cobaltites  $\text{RCoO}_3$  (R = rare earth). In these compounds only few experimental data are available, their number is certainly insufficient to estimate the crystal field parameters (CFP), hence a necessity to calculate CFP emerged and to this end we developed a method described in this paper. To check reliability of the method it is applied to orthorhombic rare earth aluminates, which possess the same crystal structure as  $\text{RCoO}_3$ . The systems  $\text{R}_x\text{Y}_{1-x}\text{AlO}_3$  are widely used for lasers, scintillator and optical recording media, rich experimental data exist for them and in several cases reliable set of CFP was deduced by fitting the theory and experiment (see e.g.<sup>1,2</sup>).

Routinely the effective Hamiltonian is written as a sum of the free ion (atomic) part  $\hat{H}_A$  and part  $\hat{H}_{CF}$  describing the crystal field:

$$\hat{H} = \hat{H}_A + \hat{H}_{CF}. \quad (1)$$

The free ion Hamiltonian is spherically symmetrical and it depends on many parameters. Approximate values of these parameters are either known, or they may be calculated, however. Details concerning the operators and parameters of  $\hat{H}_A$  are described e.g. in Ref.<sup>3</sup>.

The crystal field Hamiltonian represents more formidable problem. Within a single electron, crystal field theory it may be written as<sup>4</sup>

$$\hat{H}_{CF} = \sum_{k=0}^{k_{max}} \sum_{q=-k}^k \sum_i B_q^{(k)} \hat{C}_q^{(k)}(i), \quad (2)$$

where  $\hat{C}_q^{(k)}(i)$  is a spherical tensor operator of rank  $k$  acting on  $i$ th electron and the summation involving  $i$  is over the  $f$  electrons of R ion.  $B_q^{(k)}$  are crystal field parameters. For the  $f$  electrons maximum value  $k_{max}$  of  $k$  is equal to six, providing that cross terms of  $\hat{H}_{CF}$  between different electron configurations are neglected. Hermiticity of  $\hat{H}_{CF}$  requires  $B_{-q}^k = (-1)^q B_q^{k*}$ .

The values of  $q$  and  $k$  for which  $B_q^{(k)}$  are nonzero depend on the site symmetry. If the local symmetry of R site is low the number of CFP may be large and it is not possible *a priori* predict,

which of them will be important. When analyzing the experimental results the CFP are therefore usually determined from the best agreement of calculated and measured results using the least squares method. This is difficult, often ambiguous procedure, and it requires starting values for CFP, however. In magnetic or superconducting compounds the number of experimental data is usually insufficient to determine CFP, yet magnetic properties reflect the crystal field sensitively. There were therefore numerous attempts to estimate CFP theoretically and the effort is continuing (see Ref.<sup>5</sup> for recent survey).

In the present paper we propose to use a local Hamiltonian, expressed in the basis of the Wannier functions to calculate *ab initio* the CFP. The method is applied to determine CFP of  $R^{3+}$  ions in orthorhombic aluminates. Comparison with experiment, presented in section V, shows that the method is capable of reliable prediction of the  $4f(R)$  levels splitting by the crystal field. ‘

## II. CRYSTAL FIELD STATES OF $R^{3+}$ IONS IN ORTHORHOMBIC ALUMINATES

Rare earth aluminates in question have orthorhombically distorted perovskite structure, belonging to the  $D_{2h}^{16}$  symmetry space group. The unit cell of  $AlO_3$  contains four formula units. R ions are located on sites with  $C_s$  point symmetry and are surrounded by twelve oxygen ligands.

For R in orthorhombic aluminates a horizontal symmetry plane causes all  $B_q^{(k)}$  with odd  $q$  to be equal to zero, leaving three real  $B_0^{(k)}$  parameters ( $k=2, 4, 6$ ) and six independent complex parameters  $B_q^{(k)}$  ( $k=2, 4, 6; q=2, 4, 6; q \leq k$ ). There are thus fifteen quantities to be determined. It is known<sup>6</sup> that for site symmetries allowing complex CFP, an arbitrary rotation around the orthorhombic  $c$  axis leaves the eigenvalues of Hamiltonian (1) unchanged. This allows elimination of the imaginary part of one of the CFP, easing thus the least squares determination of  $B_q^{(k)}$  from the experimental results, at the expense that the angle of rotation remains undetermined. In a standard convention  $B_2^{(2)}$  parameter is selected to be real. In the method we propose all fifteen quantities are determined. The rotation is only invoked in section VI when comparing calculated CFP with those obtained using least squares by Duan *et al.*<sup>1</sup> and Gruber *et al.*<sup>2</sup>.

Seven  $4f$  states  $|l, m\rangle$  ( $l=3, m = \pm 3, \pm 2, \pm 1, 0$ ) of the R are split in  $C_s$  symmetry crystal field in seven singlets. The singlets are of two different types. Taking the axis of quantization along the orthorhombic  $c$  axis four of these singlets are formed by  $m = \pm 3$  and  $m = \pm 1$  states, in remaining three singlets  $\pm 2$  orbitals are mixed with  $m = 0$  state. In our analysis instead of the  $|l, m\rangle$  states the

basis of real orbitals is used

$$\begin{aligned}
|\varphi_1\rangle &= \frac{i}{\sqrt{2}}(|3, -3\rangle + |3, 3\rangle) \sim y(3x^2 - y^2) \\
|\varphi_2\rangle &= \frac{1}{\sqrt{2}}(|3, -3\rangle - |3, 3\rangle) \sim x(x^2 - 3y^2) \\
|\varphi_3\rangle &= \frac{i}{\sqrt{2}}(|3, -1\rangle + |3, 1\rangle) \sim yz^2 \\
|\varphi_4\rangle &= \frac{1}{\sqrt{2}}(|3, -1\rangle - |3, 1\rangle) \sim xz^2 \\
|\varphi_5\rangle &= \frac{1}{\sqrt{2}}(|3, -2\rangle + |3, 2\rangle) \sim z(x^2 - 3y^2) \\
|\varphi_6\rangle &= \frac{i}{\sqrt{2}}(|3, -2\rangle - |3, 2\rangle) \sim xyz; \\
|\varphi_7\rangle &= |3, 0\rangle \sim z^3
\end{aligned} \tag{3}$$

In terms of real orbitals the wave functions of the seven singlets may be written as

$$\psi_i = \sum_{j=1}^4 c_{j,i} |\varphi_j\rangle; \quad i = 1, 2, 3, 4; \quad \psi_i = \sum_{j=5}^7 c_{j,i} |\varphi_j\rangle; \quad i = 5, 6, 7. \tag{4}$$

### III. CALCULATION OF ELECTRONIC STRUCTURE AND DESCRIPTION OF METHOD

Starting step of our analysis is a standard calculation of the electronic structure of compounds in question. To this end we used the augmented plane waves + local orbital method based on the density functional theory as implemented in the WIEN2k program<sup>7</sup>. For the exchange-correlation functional the generalized-gradient approximation form<sup>8</sup> was adopted.

For the orthorhombic unit cell parameters their experimental values of  $\text{YAlO}_3$ <sup>9</sup> and  $\text{TbAlO}_3$ <sup>10</sup> were taken, but the internal crystal structure parameters were optimized by minimizing the forces acting on the atoms. Typical content  $x$  of R ions in  $\text{Y}_{1-x}\text{R}_x\text{AlO}_3$  used as laser material is  $x \sim 0.01$ - $0.03$ . In our calculations the unit cell contained 120 atoms ( $\text{RY}_{23}\text{Al}_{24}\text{O}_{72}$ , corresponding to  $x=0.0435$ ) and it retains orthorhombic symmetry. The eigenvalue problem was solved in four points of the irreducible Brillouin zone and number of basis functions was  $\sim 9200$  (corresponding to parameter  $RK_{max}=6.13$ ). The calculations were nonspinpolarized and the  $4f$  electrons of R were treated as core electrons.

Core states contribute to the spherically symmetrical component of the density only and, as a consequence, the potential on the lattice site of R in question does not contain any nonspherical component arising from the on-site R  $4f$  states. This is vital when determining the crystal field, as otherwise nonphysical interaction of the  $4f$  states with nonspherical potential they create themselves (selfinteraction) would give dominating contribution to CFP.

In the second step the  $4f(R)$  states are included in the set of valence states and the eigenvalue problem is solved with the potential obtained in calculation described above. The goal is to obtain reliable density of states projected on the  $4f$  subspace and to determine from the  $4f$  Bloch states corresponding Wannier functions. Difficult problem is the hybridization of  $4f$  states with other valence states. It depends on relative position of the energy levels and no available approximation to DFT gives the position of  $4f$  levels correctly. To deal with this problem we shift the levels using on-site orbital potentials. For atom  $i$  and state  $\alpha$  ( $\alpha = s, p, d, f$ ) the form of such potential is

$$\hat{V}_{i,\alpha} = \Delta_{i,\alpha} \hat{P}_{i,\alpha}, \quad (5)$$

where  $\Delta_{i,\alpha}$  is the magnitude of the shift and  $\hat{P}_{i,\alpha}$  is a projection operator on states  $i, \alpha$ . In aluminates the crucial is position of  $4f$  levels relative to the oxygen  $2p$  and to a lesser extent  $2s$  levels and this makes the results of our calculation dependent on a parameter

$$\Delta \equiv \Delta_{ox,2p,2s}. \quad (6)$$

The procedure indicating how  $\Delta$  can be estimated is described in the Appendix. We checked that the results are only slightly influenced by a reasonable shift of other levels (see section IV). To remove any ambiguity, the energy of oxygen levels was shifted by  $\Delta$ , no shift was applied to  $4f(R)$  states, while energy of all remaining valence states was increased by 6 Ry ( $\sim 82$  eV) preventing thus their hybridization with  $4f(R)$  orbitals.

The distance between the nearest R ions in  $RY_{23}AlO_{72}$  structure, we used is larger than 1 nm, hence the hybridization of  $4f$  states on different lattice sites is small and it is not difficult to establish correspondence between the peaks in  $4f$  DOS and the  $4f$  energy levels. In  $TbAlO_3$  the situation is more complex. The Tb-Tb distance is only 0.365 nm and  $4f$ - $4f$  hybridization leads to a considerable dispersion of the  $4f$  bands, which makes the analysis of the DOS complicated. To circumvent the problem we made the four Tb in the unit cell of  $TbAlO_3$  formally inequivalent and left  $4f$  states of three of them in the core. Even then there exists a residual dispersion, which makes the DOS peaks considerably broader compared to the DOS of  $Y_{1-x}Tb_xAlO_3$ . The situation is documented in Fig. 1.

The density of states projected on  $4f$  states makes possible to determine the energies  $\varepsilon_i$  of  $4f$  eigenstates and also their orbital composition i.e. modules  $|c_{ij}|$  of expansion coefficients in eq. (4).  $\varepsilon_i$  and  $|c_{ij}|$  may be then used to determine the crystal field on the R site. Note that if the peaks in the density of states overlap, a decomposition of the peaks on their components must precede the analysis. Such a strategy was successfully used to expose the importance of hybridization for  $Pr^{4+}$

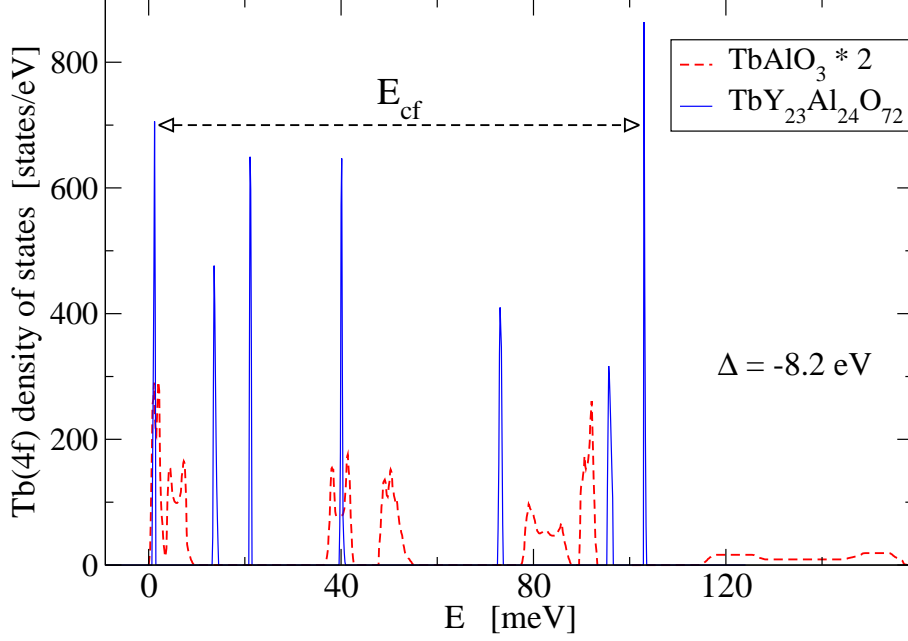


FIG. 1. (Color online)  $\text{TbAlO}_3$  and  $\text{Tb:YAlO}_3$ . Density of states projected on the  $4f$  subspace. The shift  $\Delta$  equals to  $-8.2$  eV.  $E_{cf}$  is the energy difference between the highest and lowest  $4f$  singlet state and it is used to characterize the strength of the crystal field.

ion on sites with the cubic symmetry in  $\text{PrO}_2$  and  $\text{PrBaO}_3$ <sup>11</sup>. For cubic local symmetry the energies  $\varepsilon_i$  are sufficient to determine unambiguously the CFP, but if the symmetry is lower, the  $|c_{ij}|$  must be employed as well. Our attempt to determine CFP in orthorhombic aluminates using  $\varepsilon_i$ ,  $|c_{ij}|$  and the least squares method led to several sets of results, however. The situation is reminiscent of the determination of CFP from optical spectra (see e.g. Ref.<sup>2</sup>).

In this paper we propose an elegant and unambiguous way to determine the CFP employing the Wannier functions. Wannier functions are real space counterpart of the Bloch functions and both sets are connected by a unitary transformation. In order that this transformation is unique an additional requirement on the form of Wannier functions is needed. One such requirement - maximal localization is implemented in the wannier90 package<sup>12</sup>. The interface between the WIEN2k and wannier90 was recently written by Kuneš et al.<sup>13</sup>. Among other outputs wannier90 yields also Hamiltonian  $\hat{H}_W$  in basis of the Wannier functions

$$\hat{H}_W = \hat{U}^\dagger \epsilon_k \hat{U}, \quad (7)$$

where  $\hat{U}$  is the matrix of transformation and  $\epsilon_k$  are energies of the Bloch eigenfunctions. From  $\hat{H}_W$  we extract the local Hamiltonian  $\hat{H}_{4f}$  - the seven by seven matrix consisting of the matrix elements between the  $4f$  Wannier functions centered on the R ion in question. The local Hamiltonian has the symmetry of the R site and it can be expressed as a combination of the unit operator  $\hat{I}$  and the

crystal field Hamiltonian (2)

$$\hat{H}_{4f} = E_{avg}\hat{I} + \hat{H}_{CF} = E_{avg}\hat{I} + \sum_{k,q,i} B_q^{(k)}\hat{C}_q^{(k)}(i). \quad (8)$$

In the subspace of the  $4f$  Wannier functions  $\hat{I}$  and  $\hat{C}_q^{(k)}(i)$  may be represented by  $7 \times 7$  matrices and the above equality yields the system of linear equations from which  $E_{avg}$  and  $B_q^{(k)}$  are determined.

The method was first tested by determining the crystal field parameters of  $\text{Pr}^{4+}$  ion in  $\text{PrO}_2$ <sup>5</sup>. The results were similar to those reported by us earlier<sup>11</sup>, albeit without the uncertainty in decomposition of the density of states peaks. We note that concept of the local Hamiltonian is also in the heart of CFP calculation method proposed recently by Hu *et al.*<sup>14</sup>.

#### IV. RESULTS

The calculation with the  $4f(\text{R})$  states included between the core states resulted in the band structure corresponding to an insulator with the band gap  $\sim 6$  eV. The valence band is dominated by oxygen  $2p$  states, while the bottom of the conduction band is mainly formed by  $5d(\text{R})$  and  $4d(\text{Y})$  orbitals.

When the  $4f(\text{R})$  states are treated as valence states (second step in our method) the results depend naturally on the specific  $\text{R}^{3+}$  ion and on the local geometry, but also on the value of parameter  $\Delta$ . As  $|\Delta|$  decreases hybridization of  $4f(\text{R})$  with oxygen  $2p$  states becomes larger and for  $|\Delta|$  smaller than  $\sim 2.7$  eV the gap between these levels disappears and the  $4f$  density of states becomes unresolved. The strength of the crystal field may be characterized by the difference  $E_{cf}$  of the lowest and highest  $4f$  eigenenergy (see Fig. 1).  $E_{cf}$  for all thirteen  $\text{R}^{3+}$  ions in  $\text{YAlO}_3$  and for several values of  $\Delta$  is shown in Fig. 2. As seen from this Figure the dependence of  $E_{cf}$  on the number  $N_{4f}$  of  $4f$  electrons is smooth and monotonically decreasing. The hybridization represented by the shift  $\Delta$  plays an important role.

The nonzero CFP of  $\text{R}^{3+}$  ions in  $\text{YAlO}_3$  are displayed in Figs. 3 and 4 for typical value of the shift  $\Delta = -8.2$  eV. The dependence of  $B_q^k$  on  $N_{4f}$  is again smooth, the largest energy is carried by the  $k=6, q=4$  term.

Returning to Fig. 1, we note that the crystal field in  $\text{TbAlO}_3$  is markedly stronger compared to the one in  $\text{Tb:YAlO}_3$ . This indicates a large effect of the local geometry - in both cases this geometry was determined by minimizing the forces on atoms constituting the system in question.

We remind that when obtaining above described results, the  $4f(\text{R})$  states were allowed to hybridize only with oxygen  $2p$  and  $2s$  states - hybridization with other valence states was prevented by shifting

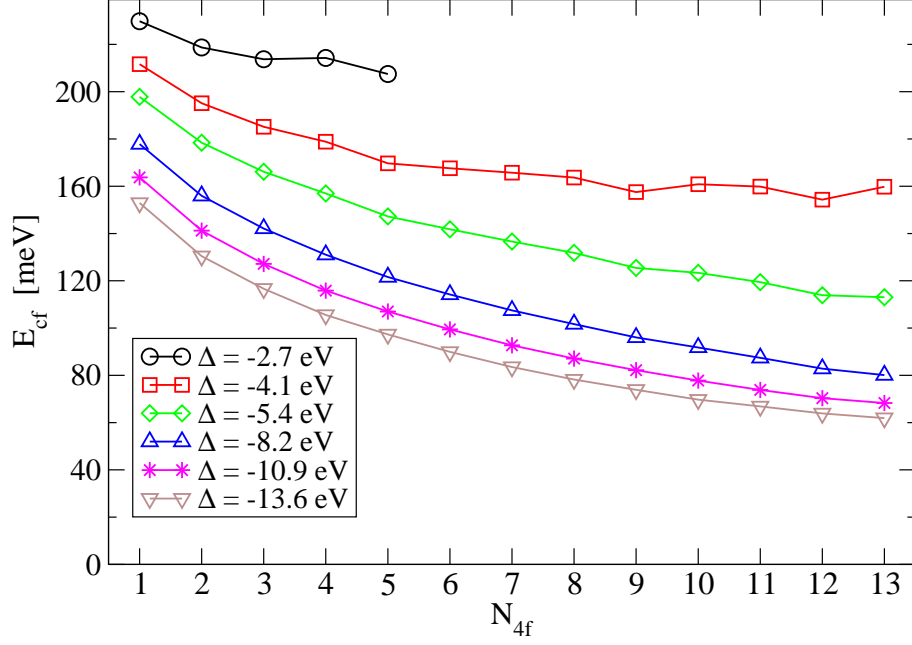


FIG. 2. (Color online). R:YAlO<sub>3</sub>. Difference  $E_{cf}$  of the lowest and the highest  $4f$  eigenenergy on number of the  $4f$  electrons for several values of the shift  $\Delta$ . Circles correspond to a calculation in which all valence states, except  $4f(R)$  were shifted by 81.6 eV (6 Ry), preventing any hybridization of the  $4f$  states. The curves in this, as well as in the following figures, serve as guides for eyes only.

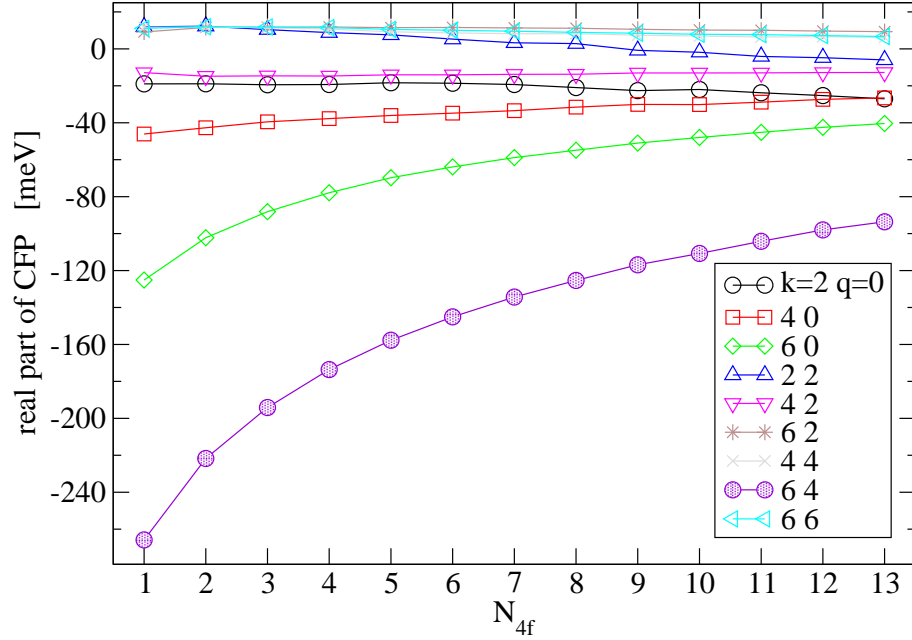


FIG. 3. (Color online). R:YAlO<sub>3</sub>. Dependence of real part of crystal field parameters on number of the  $4f$  electrons. Shift  $\Delta = -8.2$  eV.



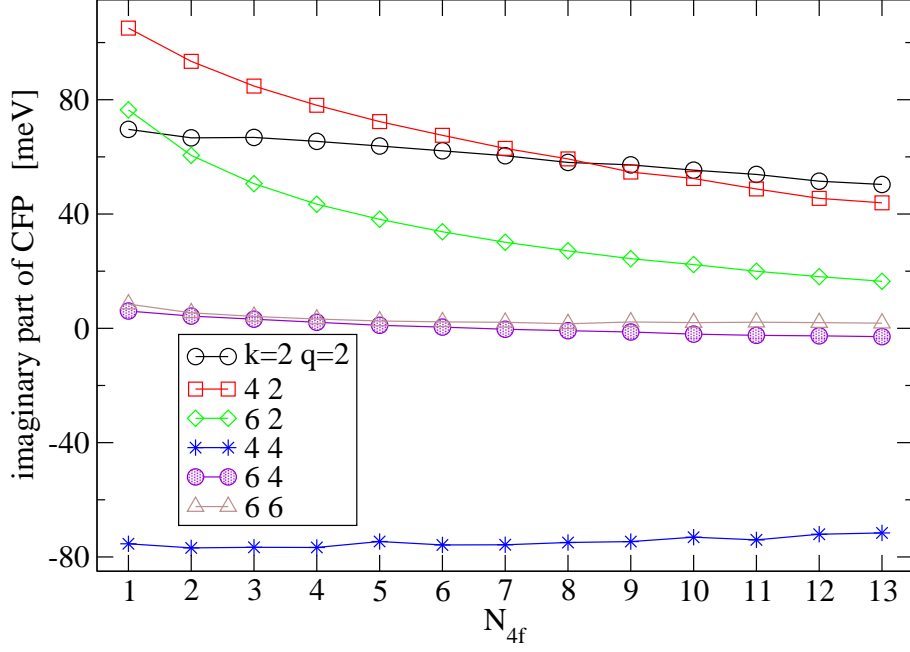


FIG. 4. (Color online). R:YAlO<sub>3</sub>. Dependence of imaginary part of crystal field parameters on number of the 4*f* electrons. Shift  $\Delta = -8.2$  eV.

their energy by  $\sim 82$  eV. For Er:YAlO<sub>3</sub> system we analyzed in details how the results are influenced by such an approximation. The eigenvalue problem was solved with  $\Delta = -8.2$  eV and energy of selected type of valence state left unshifted, allowing thus its hybridization with 4*f*(R). The importance of the hybridization may be characterized by quantity  $\Delta\varepsilon_i$

$$\Delta\varepsilon_i = (\varepsilon_i - \varepsilon_i^0)/\varepsilon_i^0, \quad (9)$$

where  $\varepsilon_i^0$  is energy of *i*th 4*f* level for all Er, Y and Al states shifted high in energy, while  $\varepsilon_i$  corresponds to calculation in which selected valence state was not shifted. The results collected in Table I show that hybridization of 4*f* states with other valence states of the cations changes the 4*f* energies by few %. The most pronounced effect has the hybridization with 5*d* states of erbium.

## V. COMPARISON WITH EXPERIMENT

In Fig. 5 the energies of Tb<sup>3+</sup> seven lowest multiplets are displayed. The energies are taken relative to the lowest energy of the multiplet in question. Experimental data<sup>2</sup> are compared with results calculated for two values of  $\Delta$ , which give the smallest deviation from the experiment.

A similar plot for the Nd<sup>3+</sup> in YAlO<sub>3</sub> is presented in Fig. 6. In this case the results are more sensitive to the value of  $\Delta$  and calculations for  $\Delta = -4.1$ ,  $-8.2$  and  $-10.9$  eV are confronted with the

state	Er			Y			Al	
	s	p	d	s	p	d	s	p
2	2.9	2.2	4.6	5.5	2.6	3.4	-2.0	0.7
3	2.0	1.6	7.4	3.4	1.6	3.7	-4.7	-2.4
4	1.1	0.2	2.8	1.0	1.0	-0.2	0.9	0.7
5	-1.7	1.0	-5.5	1.3	1.0	0.4	1.1	1.3
6	0.5	1.7	-5.3	2.2	1.9	1.8	1.7	1.8
7	-0.8	1.9	0.9	2.0	2.1	1.4	1.9	1.7

TABLE

9).

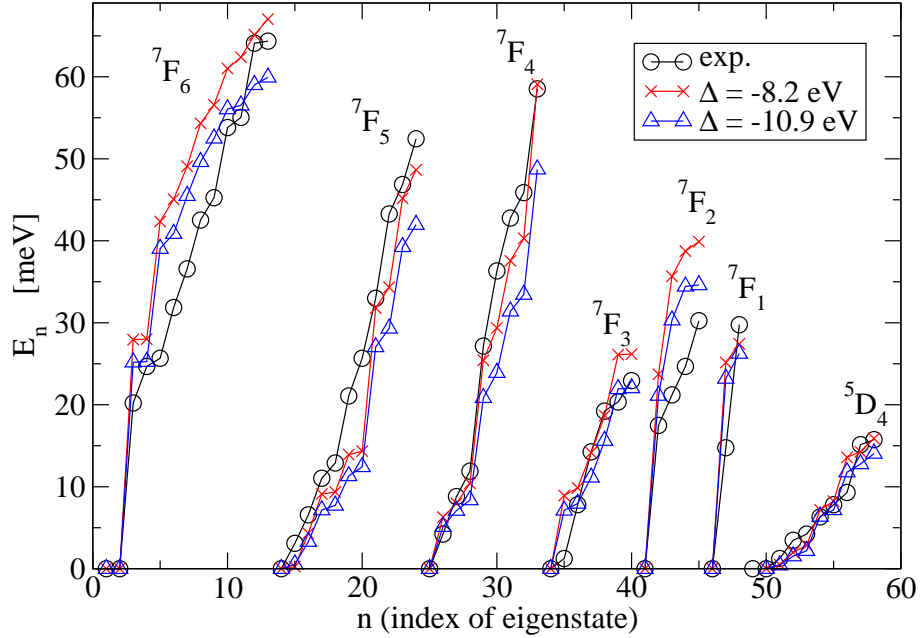


FIG. 5. (Color online)  $\text{TbAlO}_3$ . Energies of  $\text{Tb}^{3+}$  eigenstates taken relative to the lowest energy of the multiplet. The experimental data were determined by Gruber *et al.*<sup>2</sup>.

experiment<sup>1,20</sup>. In addition the data obtained with all, but  $4f$  states displaced by 6 Ry ( $\sim 82$  eV), which prevented the hybridization, are also included.

As the third example we consider  $\text{Er}^{3+}$  ion in  $\text{YAlO}_3$ . As seen in Fig. 7 the experimental data for the four lowest multiplets are in very good agreement with the calculation in which the shift parameter  $\Delta$  is equal to -8.2 eV. For  $\text{Er}:\text{YAlO}_3$  and  $\Delta = -8.2$  eV we calculated the mean square deviation  $\sigma$  of the experimental and calculated splittings:

$$\sigma = \frac{1}{n_{exp}} \sum_{j=1}^{n_{exp}} \sqrt{E_{j,exp.}^2 - E_{j,calc.}^2}, \quad (10)$$

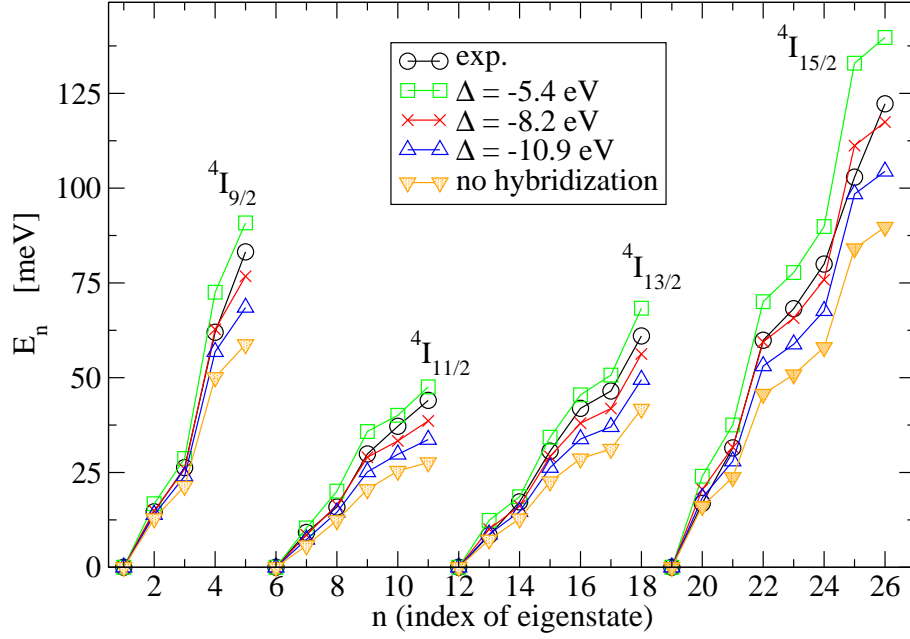


FIG. 6. (Color online)Nd:YAlO<sub>3</sub>. Energies of Nd<sup>3+</sup> eigenstates taken relative to the lowest energy of the multiplet. The experimental data were determined by Kaminskii<sup>20</sup> and Duan *et al.*<sup>1</sup>.

where  $n_{exp}$  is the number of experimentally observed levels in the  $j$ th set and the energies are again taken relative to the lowest level in the set (the sets correspond to the  $|L, S, J, M_J\rangle$  multiplets, with the exception of the set 14, which combines  $^2K_{13/2}$ ,  $^2P_{1/2}$  and  $^4G_{5/2}$  multiplets). In Fig. 8 the mean square deviation is displayed for the lowest 19 Er<sup>3+</sup> sets. With the exception of sets 14, 16 and 19 values of  $\sigma$  indicate a fair agreement of experiment and calculation. We note that in these three cases not all levels were observed experimentally, while for the remaining 16 multiplets all levels were detected.

## VI. DISCUSSION

The results presented in Figs. 2, 6 and 7 show convincingly that the hybridization of  $4f$  states is important. Our semiempirical estimation of the parameter  $\Delta$ , which reflects its strength, amounts to -4.3, -11.5 and -5.1 eV for Nd, Tb and Er, respectively (see the Appendix). This qualitatively agrees with  $\Delta$  for which the calculated positions of the energy levels fit the experiment best (optimal  $|\Delta|$  being in limits 5-8, 8-11 eV for Nd and Tb and  $\sim 8$  eV for Er).

In order to compare calculated CFP with those obtained by least squares fit to the optical spectra<sup>1,2</sup>, the rotation angle  $\alpha$  must be first calculated, as explained in section II. It is straight-

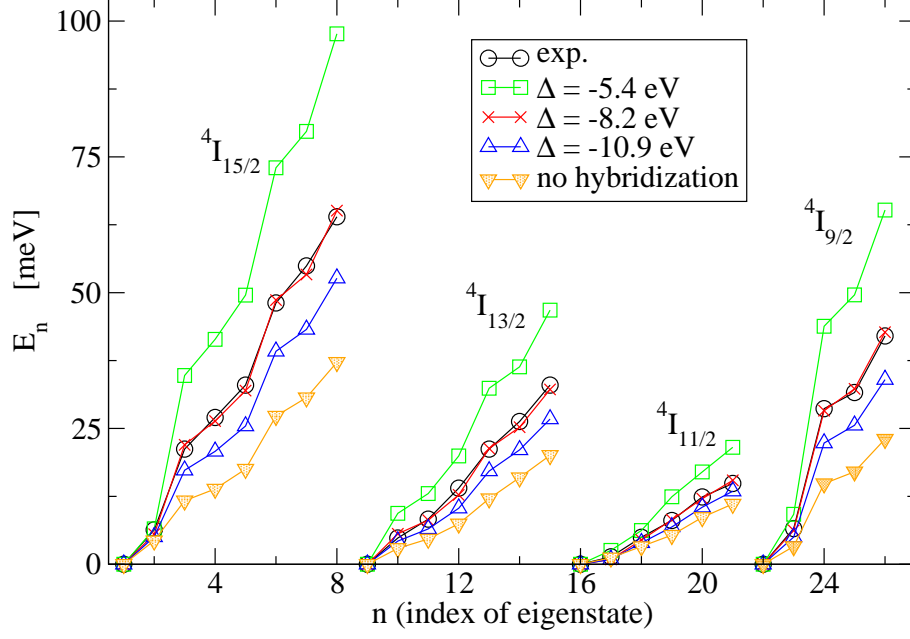


FIG. 7. (Color online)Er:YAlO<sub>3</sub>. Energies of Er<sup>3+</sup> eigenstates taken relative to the lowest energy of the multiplet. The energy levels are calculated with the crystal field splitting parameter  $\Delta = -8.2$  eV.

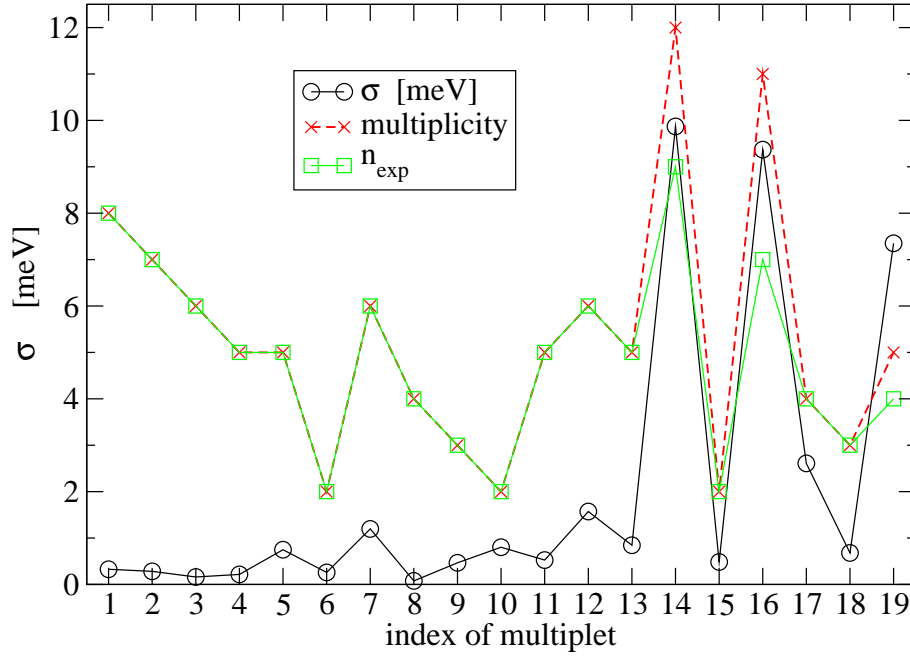


FIG. 8. (Color online)Er:YAlO<sub>3</sub>. The mean square deviation  $\sigma$  of the experimental splittings and splittings calculated with  $\Delta = -8.2$  eV. Crosses correspond to the multiplicity of the set of levels, number of levels observed experimentally  $n_{exp}$  is denoted by squares. The experimental data were determined by Donlan and Santiago<sup>21</sup> and Duan *et al.*<sup>1</sup>.

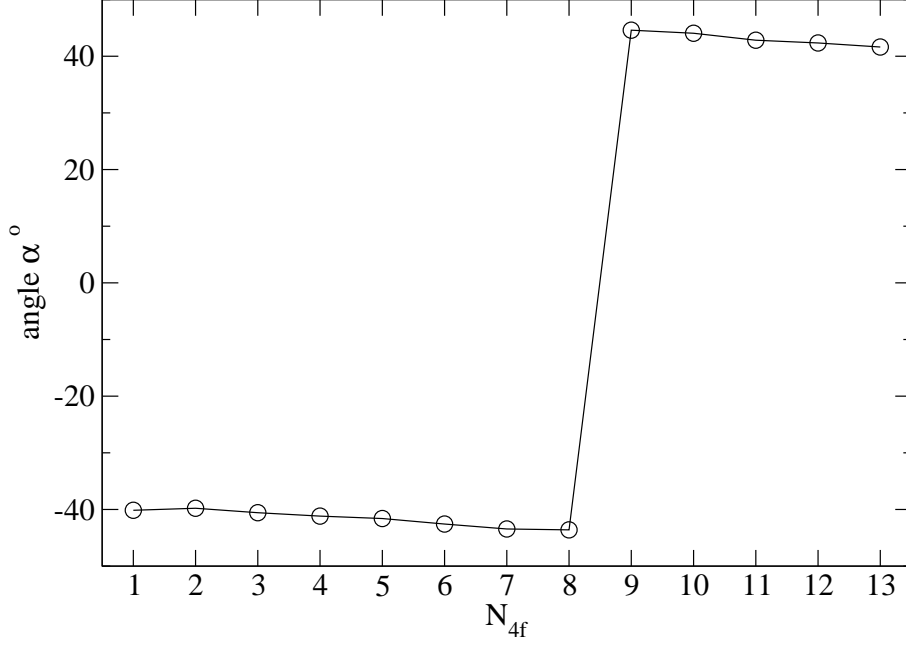


FIG. 9. (Color online) Angle of rotation around orthorhombic  $c$  axis.

forward to show that if imaginary part of  $B_2^2$  in rotated system is to be zero,  $\alpha$  is given by

$$\alpha = -\arctg(B_{2,imag}^2/B_{2,real}^2), \quad (11)$$

where  $B_{2,imag}^2$ ,  $B_{2,real}^2$  are imaginary and real parts of  $k=2$ ,  $q=2$  CFP in orthorhombic coordinate system. As seen from Figs. 3, 4 for  $\Delta = -8.2$  eV  $B_{2,imag}^2$  is large and positive for all  $R^{3+}$  ions, while  $B_{2,real}^2$  is small and positive for lighter R, changing the sign for  $R = Dy$ . The dependence of  $\alpha$  on  $N_{4f}$  is displayed in Fig. 9. As seen from this Figure  $\alpha(N_{4f})$  change the sign, which leads to a discontinuity of  $B_q^k(N_{4f})$  dependence despite the fact that in original orthorhombic system the crystal field parameters change continuously with  $N_{4f}$ . This concerns all  $q=2$  and  $q=4$  terms and for this reason it is more informative to compare absolute values of  $B_q^k$ , rather than to compare separately their real and imaginary parts. Such comparison for  $Nd^{3+}$  and  $Er^{3+}$  ions in  $YAlO_3$  and for  $Tb^{3+}$  ion in  $TbAlO_3$  is given in Table II. The correspondence between calculated CFP and those obtained by the least squares fit of the experiment is satisfactory. In particular the  $k=6$ ,  $q=4$  term carries the largest energy and the crystal field decreases with increasing number of  $4f$  electrons. CFP determined by fitting the optical spectra suffer from the ambiguity connected with numerous local minima of the least squares method applied in the 14 dimensional space of variables. In this connection we return to the  $Er:YAlO_3$  case (Fig. 8) in which the agreement between our calculation and the energy levels fixed using optical spectra was significantly worse for the level sets 14, 16, 19, for which not all the levels were detected. The assignment of measured levels in the least squares

k	q	Nd <sup>3+</sup> in YAlO <sub>3</sub>		Tb <sup>3+</sup> in TbAlO <sub>3</sub>		Er <sup>3+</sup> in YAlO <sub>3</sub>	
		calc.	exp. (a)	calc.	exp. (b)	calc.	exp. (a)
2	0	157	154	355	757	192	178
4	0	319	541	114	469	233	134
6	0	711	671	621	503	364	453
2	2	545	578	546	262	436	490
4	2	694	967	544	181	407	499
6	2	419	512	256	476	180	208
4	4	625	682	696	375	599	627
6	4	1566	1611	1096	1235	840	808
6	6	101	132	210	512	65	78

TABLE II. Comparison of absolute values of crystal field parameters calculated with the shift  $\Delta=-8.2$  eV with those obtained by Duan *et al.*<sup>1</sup> (a) and Gruber *et al.*<sup>2</sup> (b) by least squares fit to optical spectra. All CFP are in units of  $\text{cm}^{-1}$ .

method is far from being unique and the results of our calculation may serve as a useful seed values for it.

There are several limitations of the method we suggest for the CFP calculation. In order to prevent the selfinteraction, the  $4f$  hybridization with other valence states was treated in a nonselfconsistent way. This may be a problem for  $\text{Ce}^{3+}$  ion and for compounds with tetravalent R ions, where the hybridization is known to be significant. For trivalent R heavier than Ce, the effect is likely to be small.

Another approximation is connected with the assumed single electron character of the crystal field Hamiltonian. Obviously the closer  $|L, S, J, M_J\rangle$  multiplet is to the top of the valence band, the stronger is the hybridization. This leads to CFP being different in different multiplets, the effect which is included if the concept of correlation crystal field<sup>23,24</sup> is used, or if CFP are allowed to be energy dependent. Taking into account that different multiplets of  $\text{Nd}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Er}^{3+}$  are well described by single CFP set (section V), CFP energy dependence and correlation crystal field play only a minor role in cases considered here.

While the above discussed crystal field Hamiltonian yields satisfactorily the positions of  $4f$  levels, it gives no information on the intensity of  $4f-4f$  transitions and the Judd-Ofelt theory<sup>25</sup> must be used to this end. It was suggested recently by Hu *et al.*<sup>14</sup> that concept of 'local dipolar operator', which is similar to the concept of local Hamiltonian, may be used instead of the Judd-Ofelt theory.

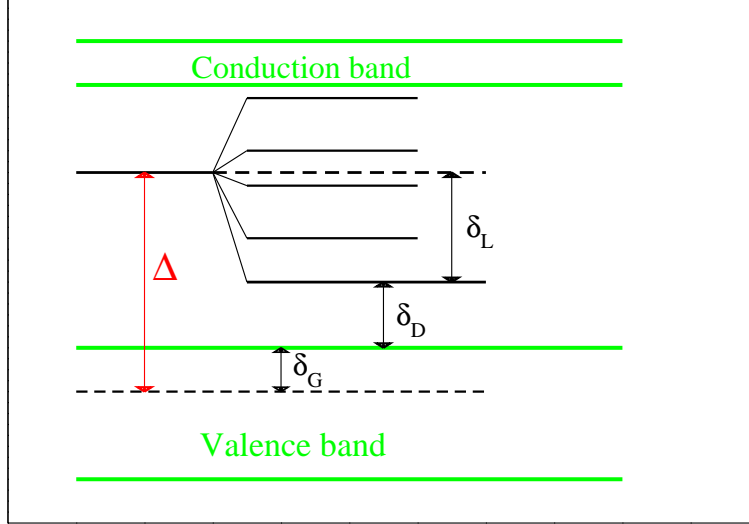


FIG. 10. (Color online) Scheme of levels in rare earth containing oxides.

Very recently a part, which allows to treat optics, was added to the wien2wannier package<sup>13,22</sup>. It is relatively straightforward to extract from that part the 'local dipolar operator' expressed in the basis of Wannier functions. The generalization of the method we propose here will then allow to determine both positions of  $4f$  levels and  $4f - 4f$  transition intensities in a single step.

## VII. CONCLUSIONS

In conclusion we presented a method to calculate the CFP that is fully *ab initio* except a single parameter  $\Delta$  which corresponds to energy difference between the unsplit  $4f(R)$  and oxygen valence levels.  $\Delta$  is estimated using independent experimental data and its estimation may be useful when explaining other experiments e.g. the luminescence. The viability of the method is demonstrated by the good agreement between the calculated and experimentally observed crystal field splitting of the  $|L, S, J, M_J\rangle$  multiplets of  $Nd^{3+}$ ,  $Tb^{3+}$  and  $Er^{3+}$  ions. The method may become a valuable tool to interpret the experiments, especially after the determination of  $4f - 4f$  transition probabilities will be added as described in section VI.

### Appendix A: Energy of rare earth $4f$ level relative to oxygen $2p$ states

The scheme of energy levels in the rare earth aluminates is shown in Fig. 10. As seen from this Figure the shift  $\Delta$  may be written as a sum of three contributions

$$\Delta = \delta_L + \delta_D + \delta_G, \quad (A1)$$

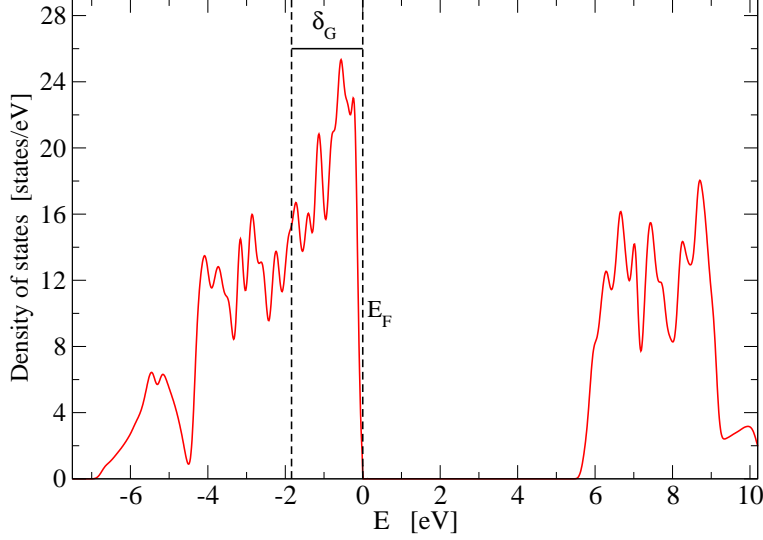


FIG. 11. (Color online) Total density of states of  $\text{TbY}_{23}\text{Al}_{24}\text{O}_{72}$  with  $4f$  states included between the core states. Dashed line corresponds to the center of gravity of the valence band, Fermi energy is at zero.

where  $\delta_L$  is difference of unsplit  $4f$  level energy and the energy of the ground  $|L, S, J, M_J\rangle$  multiplet.  $\delta_D$  is difference of the ground multiplet energy and energy of the top of valence band. Finally  $\delta_G$  is obtained by subtracting energies of the top and center of gravity of this band.

The valence band is dominated by the oxygen  $2p$  states, width of this band in the orthorhombic aluminates is  $\sim 6.9$  eV and the energy difference  $\delta_G$  is  $\sim 1.84$  eV (Fig. 11).

In a series of papers Dorenbos collected and analyzed the spectroscopic data concerning the  $4f$  electron states of rare earth substitutions in transition metal complex compounds (see<sup>17</sup> and references therein). In particular the energy difference, we denote as  $\delta_D$  was determined.  $\delta_D$  depends on the compound in question, but as discussed by Rogers et al.<sup>18</sup> the difference  $\delta_D(\text{R}) - \delta_D(\text{R}')$  is to a good approximation compound independent. In Fig. 12  $\delta_D(\text{R}) - \delta_D(\text{Gd})$  is displayed for all trivalent rare earth ions. The data were adopted from Fig. 1 of reference<sup>18</sup>. In seven different oxides for which Dorenbos et al.<sup>17</sup> analyzed the spectroscopic data the ground  $^8S_{7/2}$  multiplet of  $\text{Gd}^{3+}$  lies below the top of the valence band,  $\delta_D(\text{Gd})$  is thus negative with values ranging from -5 to -2.5 eV.

To determine the energy difference  $\delta_L$  between the unsplit  $(4f)^n$  and the lowest  $|L, S, J, M_J\rangle$  multiplet we used the 'lanthanide' program<sup>15</sup> with parameters of Carnall et al.<sup>19</sup>. The dependence of  $\delta_L$  on the type of trivalent rare earth is shown in Fig. 12.

Finally adding  $\delta_D(\text{R}) - \delta_D(\text{Gd})$ ,  $\delta_L(\text{R})$ ,  $\delta_G$  with minimal and maximal values of  $\delta_D(\text{Gd})$  yields the range in which  $\Delta(\text{R})$  should lie (Fig. 13).



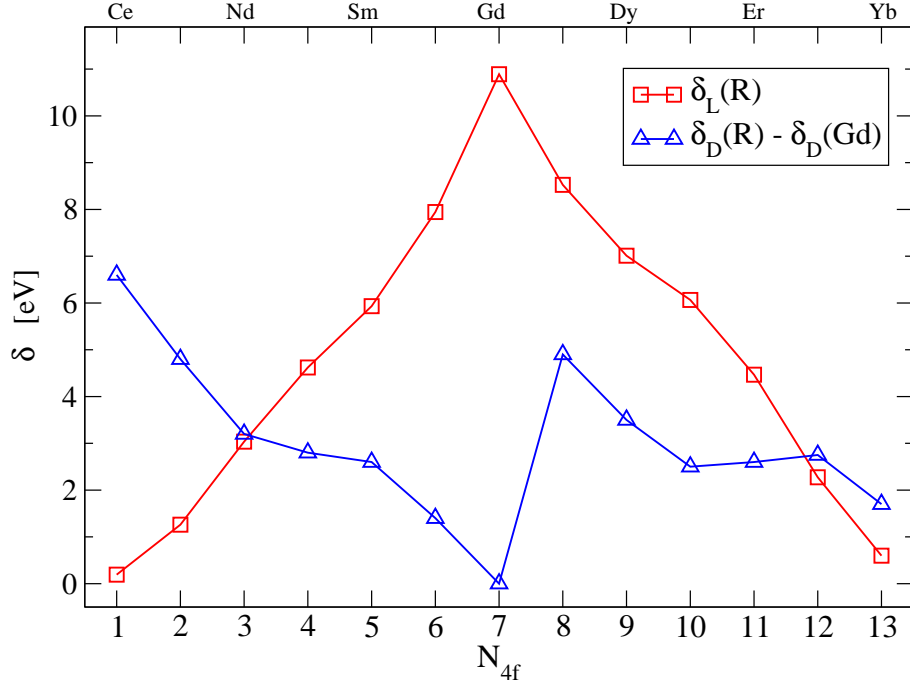


FIG. 12. (Color online) Energy differences  $\delta_L(R)$  between the unsplit  $4f$  level and the ground multiplet (open circles), and  $\delta_D(R)$  of the ground multiplet and the top of the valence band. The data for  $\delta_D(R)$  are relative to  $\delta_D(Gd)$  and were adopted from ref<sup>18</sup>

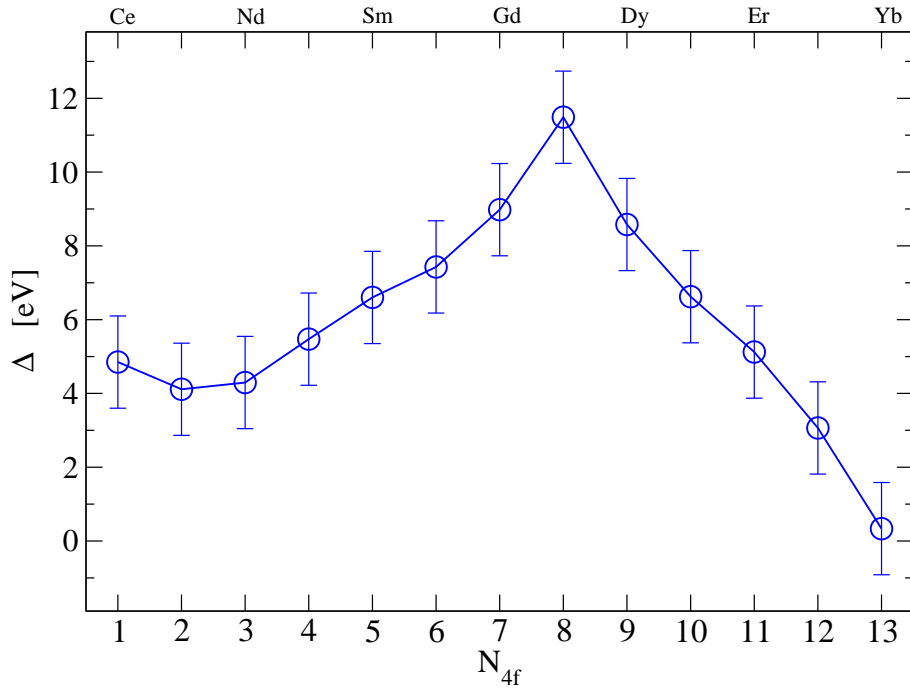


FIG. 13. (Color online) Minimum and maximum of the energy difference  $\Delta$  between the unsplit  $4f$  level and the center of gravity of the valence band.  $n$  is number of electrons of trivalent rare earth ion.

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